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Abstract

Motivation. This report was motivated by a recent paper (T. Došlić, Perfect Matchings in Lattice Animals and Lattice Paths with Constraints, *Croat*. *Chem*. *Acta* **2005**, *78*, 251–259), and an idea of expressing the number of Kekulé structures of damaged benzenoid parallelograms by a two–parameter formula, the parameters being the width and length of the parallelogram. The number of Kekulé structures appears to be an important quantity for predicting the stability of benzenoid structures.

Method. All formulas were derived by using the combinatorial enumeration based on the binomial coefficients.

Results. Formulas for the Kekulé–structure counts of damaged benzenoid parallelograms are derived. Perimeter–edges are indicated whose removal produces the least or the most damaged benzenoid parallelograms.

Conclusions. The number of Kekulé structures of damaged benzenoid parallelograms is expressible in terms of the width and length of parent structures.

Keywords. Benzenoid parallelogram; carbon network; combinatorial enumeration; damaged benzenoid parallelogram; Kekulé structure count.

1 INTRODUCTION

In continuation of our studies on planar, spherical and cylinder–like hexagonal networks [*e.g*., 1–5], we here report the enumeration of Kekulé structures in damaged benzenoid parallelograms. The two–parameter formula for counting the Kekulé–structures of benzenoid parallelograms, which is based on their width and length, is known for many years [6]. The aim of the present report is to investigate whether the same two parameters can be used to derive simple combinatorial formulas for counting Kekulé structures in benzenoid parallelograms when they lose their regular structures due to some physical or chemical damage imposed on the perimeter–edges [7,8]. In chemical

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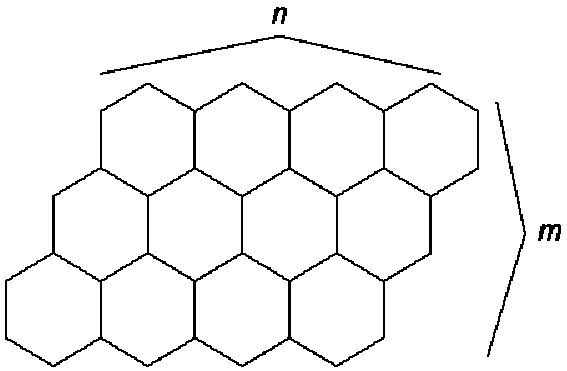
language, by the notion 'damaged benzenoid hydrocarbon' we mean that one bond (or more bonds) of a benzenoid hydrocarbon ceases to participate to the conjugated system.

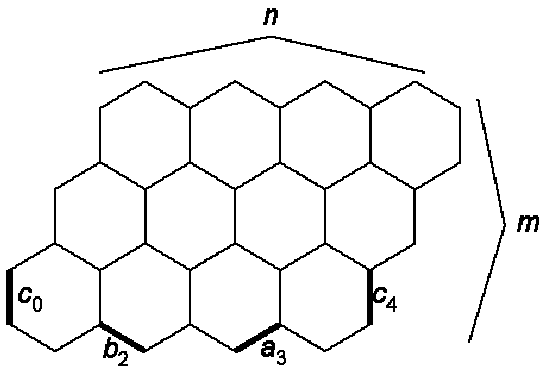
A legitimate question to ask is why one needs the number of Kekulé structures? The answer is that they are used in a number of approaches to account for the stability of benzenoids [*e.g.*, 9–13], the simplest approach being by Swinborne–Sheldrake *et al*. [14].

2 DAMAGED BENZENOID PARALLELOGRAMS

Let G be any benzenoid graph [15]. Denote by $\kappa(G)$ the number of Kekulé structures of G. Let also $m,n \geq 2$. Let $B_{m,n}$ be a benzenoid parallelogram with m rows and n columns [16]. The example for $B_{3,4}$ is given below:



In the recent paper by Došlić [17], it is shown that the number of all Kekulé strucutres of $B_{m,n}$ is equal to the number of non–decreasing functions from $f:\{1,...,m\} \to \{0,...,n\}$, *i.e*, it is equal to $\binom{m+n}{m}$. Denote by a_k the upward oriented edge in the lowest row in the $k-th$ hexagon; denote by b_k the downward oriented edge in the lowest row in the $k-th$ hexagon and denote by c_k the vertical edge in the lowest row that has k hexagons to the left. The example of a_3 and b_2, c_0 and c_4 are given below:



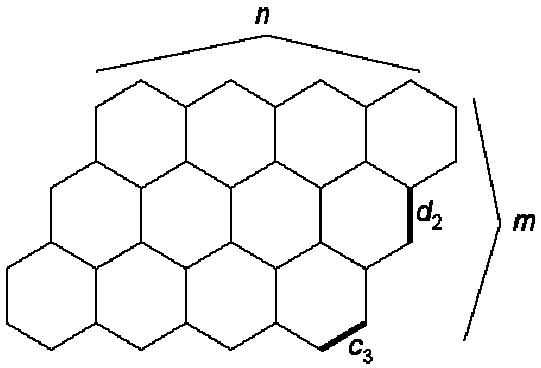
Moreover, from the observation given in Došlić's paper [17], it follows that the number of Kekulé structures not containing double–bond a_k is equal to the number of non–decreasing functions from $f:\{1,...,m\}\to\{k,...,n\}$ (because the vertical double–bond in the lowest row cannot be c_0, $c_1,\ldots,c_{k-1}$). Obviously this number is equal to the number of non–decreasing functions $f:\{1,...,m\}\to\{0,...,n-k\}$, *i.e.*, it is equal to $\binom{m+n-k}{m}$. Hence, we may conclude that

$$\kappa\left(B_{m,n}-a_k\right)=\binom{m+n-k}{m}$$

Note that each structure contains either a_k or b_k. Therefore,

$$\kappa\left(B_{m,n}-b_k\right)=\binom{m+n}{n}-\binom{m+n-k}{m}$$

Similarly, denote c_k and d_k as on the following figure:



Using symmetry, one obtains:

$$\kappa\left(B_{m,n}-c_k\right)=\binom{m+n-k}{n}$$

and

$$\kappa\left(B_{m,n}-d_k\right)=\binom{m+n}{n}-\binom{m+n-k}{n}$$

Note that $a_n=c_m$ and hence naturally,

$$\kappa\left(B_{m,n}-a_n\right)=\binom{m+n-m}{n}=1=\binom{m+n-n}{m}=\kappa\left(B_{m,n}-a_m\right)$$

Completely analogously the problem can be solved if the damaged edge is located on the left or upper perimeter of the benzenoid.

Now, let us find out what perimeter–edge is 'the most important not to be damaged', *i.e.*, we

want to find perimeter–edge e such that $\kappa\left(B_{m,n}-e\right)$ is minimal. According to the above analyses, one has to find the minimum of the following set:

$$S_1=\left\{\begin{pmatrix}m+n-k\\ m\end{pmatrix},\begin{pmatrix}m+n\\ m\end{pmatrix}-\begin{pmatrix}m+n-k\\ m\end{pmatrix}:\ k=1,\ldots,n\right\}\cup\left\{\begin{pmatrix}m+n-k\\ n\end{pmatrix},\begin{pmatrix}m+n\\ n\end{pmatrix}-\begin{pmatrix}m+n-k\\ n\end{pmatrix}:\ k=1,\ldots,m\right\}$$

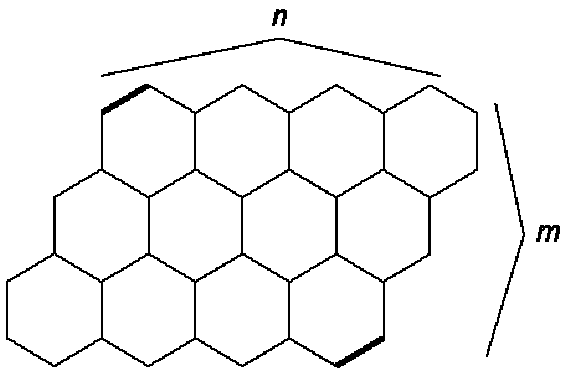
Note that $\begin{pmatrix}x\\ y\end{pmatrix}$ is strictly increasing function in x. Hence, minimum of the set S_1 is equal to the minimum of the set:

$$S_2=\left\{\begin{pmatrix}m\\ m\end{pmatrix},\begin{pmatrix}m+n\\ m\end{pmatrix}-\begin{pmatrix}m+n-1\\ m\end{pmatrix}\right\}\cup\left\{\begin{pmatrix}n\\ n\end{pmatrix},\begin{pmatrix}m+n\\ n\end{pmatrix}-\begin{pmatrix}m+n-1\\ n\end{pmatrix}\right\}$$

Recall that: $\begin{pmatrix}x\\ y\end{pmatrix}=\begin{pmatrix}x-1\\ y\end{pmatrix}+\begin{pmatrix}x-1\\ y-1\end{pmatrix}$. Therefore:

$$S_2=\left\{1,\begin{pmatrix}m+n-1\\ m-1\end{pmatrix},\begin{pmatrix}m+n-1\\ n-1\end{pmatrix}\right\}$$

Hence, the benzenoid can be damaged the most by deletion either one of the two perimeter–edges indicated in the following figure:



Let us now find out what perimeter–edge is ‘the least important not to be damaged’, *i.e.*, we want to find perimeter–edge e such that $\kappa\left(B_{m,n}-e\right)$ is maximal. Hence, we search for the maximum of the set:

$$S_1=\left\{\begin{pmatrix}m+n-k\\ n\end{pmatrix},\begin{pmatrix}m+n\\ n\end{pmatrix}-\begin{pmatrix}m+n-k\\ n\end{pmatrix}:\ k=1,\ldots,m\right\}\cup\left\{\begin{pmatrix}m+n-k\\ m\end{pmatrix},\begin{pmatrix}m+n\\ m\end{pmatrix}-\begin{pmatrix}m+n-k\\ m\end{pmatrix}:\ k=1,\ldots,n\right\}$$

Analogously as before, this reduces to finding the maximum of the set:

$$S_3 = \left\{ \binom{m+n-1}{n}, \binom{m+n}{n} - \binom{m+n-m}{n} \right\} \cup \left\{ \binom{m+n-1}{m}, \binom{m+n}{m} - \binom{m+n-n}{m} \right\}.$$

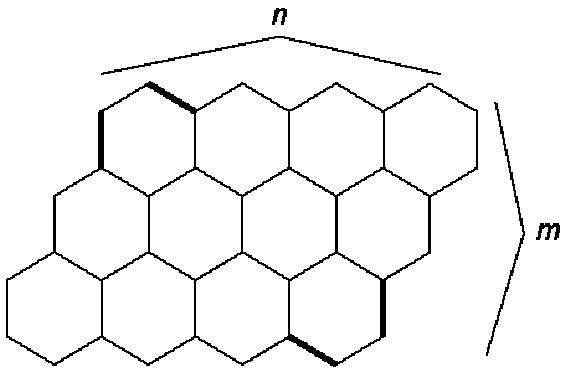
Hence, we need to find the maximum of the set $\left\{ \binom{m+n-1}{n}, \binom{m+n-1}{m}, \binom{m+n}{n} - 1 \right\}$. Note that:

$$\binom{m+n}{m} - 1 = \binom{m+n-1}{m} + \binom{m+n-1}{m-1} - 1 > \binom{m+n-1}{m}$$

$$\binom{m+n}{m} - 1 = \binom{m+n}{n} - 1 = \binom{m+n-1}{n} + \binom{m+n-1}{n-1} - 1 > \binom{m+n-1}{n}.$$

Therefore, the maximum is $\binom{m+n}{m} - 1$.

As a result, we conclude that the benzenoid parallelogram is the least damaged by deletion of the following perimeter–edges:



3 CONCLUDING REMARKS

The benzenoid paralleograms are special cases of the hexagonal carbon network immersed in the sea of π–electrons. They came into the focus of research after discovery of fullerenes and the role of graphite in their production, *e.g.*, [18]. Many classes of benzenoids have been explored by a number of authors, most notably by Cyvin and Gutman [16,19]. But discussions on the damaged benzenoids are rather rare in the vast literature on this class of compounds. Here we give combinatorial formulas for counting Kekulé structures in defective benzenoid parallelograms. We also pointed to bonds whose removal causes the least or the most damage of benzenoid parallelograms.

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